Picloram Movement in an Appalachian Hardwood Forest Watershed[1]

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ABSTRACT

Picloram (4-amino-3,5,6-trichloropicolinic acid) was applied at a rate of 5.0 kg ha^{-1} acid equivalent to 4 ha of the 28-ha Watershed 19, Coweeta Hydrologic Laboratory in western North Carolina. The herbicide was broadcast manually as a pellet formulation (10% acid equivalent) in May 1978. The objective was to eliminate a poor-quality mixed oak overstory and rhododendron (*Rhododendron maximum* L.)-laurel (*Kalmia latifolia* L.) understory prior to planting white pine (*Pinus strobus* L.). Picloram residues in samples from an Umbric Dystrochrept soil peaked in concentration in the upper 0.07 m at 11.58 mg kg^{-1}, had a half-life of about 4 weeks, and declined to near detection limits 28 weeks after application. Soil solution contained the highest picloram levels at 0.6 m (peak of 350 mg m^{-3}). Picloram residues were detected in soil solution 1.2 m into the soil, but concentrations were < 25 mg m^{-3}, and persisted for only 60 weeks. Intensive sampling of two springs detected trace levels for a period of 18 d. Only sporadic, low-level picloram residues were detected in streamflow from nested 10-ha and 28-ha watersheds during a 70-week period. Use of the herbicide picloram did not affect the quality of streamflow from Watershed 19 for domestic or agricultural purposes.

Additional Index Words: water quality, herbicide, groundwater, streamflow.

Many ridge sites in the southern Appalachian Mountains currently contain low-quality mixed hardwoods, rhododendron (*Rhododenron maximum* L.) and mountain laurel (*Kalmia latifolia* L.) in thickets of up to 18 000 stems ha^{-1}. These sites could support more productive stands of fast-growing eastern white pine (*Pinus strobus* L.) (Swank and Schreuder, 1973; Neary et al., 1984). Conversion with mechanical or manual methods is difficult and costly on these sites. Furthermore, prolific hardwood sprouting creates severe competition for newly planted pine seedlings. Prior research in the Appalachians has shown that effective competition control is necessary for successful conversion from scrub hardwoods to white pine (Swank and Miner, 1968). A promising alternative conversion technique is the use of herbicides such as picloram (4-amino-3,5,6-trichloropicolinic acid). This herbicide is manufactured by Dow

This publication reports research involving pesticides. It does not imply that the uses discussed here have been registered. All uses of pesticides must be registered by appropriate state and/or federal agencies before they can be recommended.

CAUTION: Pesticides can be injurious to humans, domestic animals, desirable plants, and fish or wildlife—if they are not handled or applied properly. Use all pesticides selectively and carefully. Follow recommended practices for the disposal of surplus pesticides and pesticide containers.

Chemical Company, Midland, MI, as the potassium salt in a 10% acid equivalent granule formulation. (Use of trade and corporation names does not constitute endorsement by USDA but is provided as a reference.) However, the water quality impacts of using picloram to convert low-quality hardwood stands to white pine are not fully understood.

Picloram has proven to be an effective herbicide for many herbicide-resistant woody plant species at rates less than the maximum-labeled rate of 9.5 kg ha^{-1} (Foy, 1975; NRCC, 1974; Peevey, 1970; Neary et al., 1979). In addition, the granular formulation is easy to apply and control. Its low toxicity to a wide range of animal species reduces the potential impacts of picloram on nontarget organisms (NRCC, 1974; Sergeant et al., 1971; Somers et al., 1974; Woodward, 1976).

Picloram losses by volatilization are negligible because of its low vapor pressure (Foy, 1975). Photodegradation occurs only when picloram is exposed directly to sunlight in aqueous solutions or on soil surfaces (Merkle et al., 1967). Leaching of picloram through the soil resembles a spreading and subsiding wave similar to nitrate and chloride. In most soils, the herbicide stays within the upper 1.2 m, but leaching can occur to greater depths in sandy soils, in soils prone to extensive cracking, or where large macropores and root channels exist (Phillips and Feltner, 1972; Rao et al., 1974).

Picloram's leaching through soil is a function of its high solubility and low reversible adsorption potential (Farmer and Aochi, 1974). Sorption is controlled primarily by soil organic carbon content, but also increases with decreasing pH and increased hydrated iron and aluminum oxide contents (Grover, 1968; Rao and Davidson, 1980; Karickhoff, 1981). Sorption of picloram can be described by the Freundlich isotherm. Several mechanisms controlling partitioning of picloram molecules between sorbed and solution phases have been proposed, but are not fully understood (Biggar and Cheung, 1973; NRCC, 1974). A more complete discussion of absorption-desorption phenomena is provided by Rao and Davidson (1980).

Since picloram formulated as both the potassium and amine salts has a high water solubility (> 400 000 g m^{-3} at 25°C), a major environmental concern with the use of picloram is possible contamination of surface water or groundwater used for irrigation. Crops such as alfalfa (*Medicago falcata* L.), sugar beet (*Beta vulgaris* L.), soybean [*Glycine max* (L.) Merr.], tomato (*Lycopersicon esculentum* Mill), and cotton (*Gossypium* spp.) are very sensitive to picloram in the range of 1 to 160 mg m^{-3} (Baur et al., 1972; Davis et al., 1968). Misapplication of picloram herbicides to surface waters or overuse in humid regions where leaching is a potential problem could lead to significant adverse nontarget impacts.
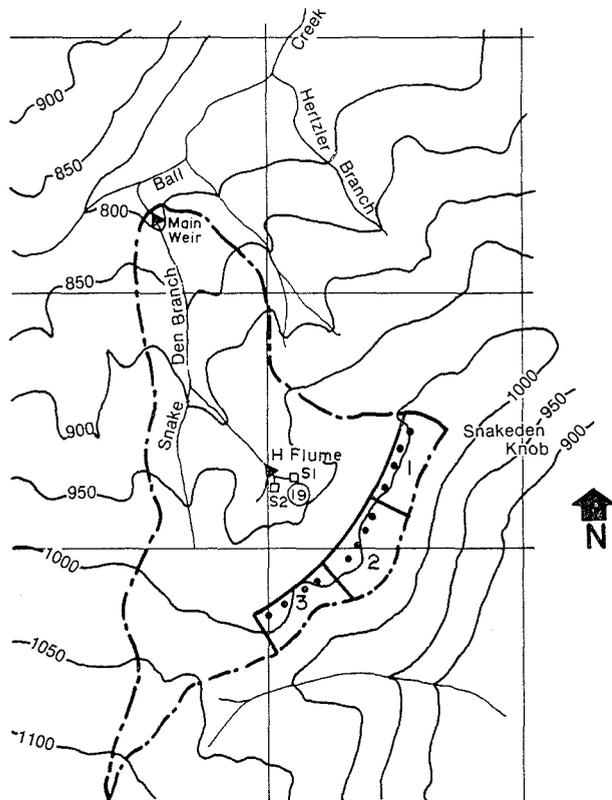
Concentrations of picloram detected in surface runoff or streamflow have varied widely in different studies. Applications of sprays at 1.1 kg ha^{-1} acid equivalent (ae) to cropland and rangeland in the South

Fig. 1. Picloram application area, Watershed 19, Coweeta Hydrologic Laboratory, Nantahala National Forest, NC.

Plot Treatment

1	5.0 kg ha⁻¹ picloram
2	5.0 kg ha⁻¹ picloram
3	Control

• Lysimeter cluster

Scale: 1 cm = 72 m

have produced peak picloram concentrations in surface water of 90 to 2170 mg m⁻³ (Scifres et al., 1971; Trichell et al., 1968; Baur et al., 1972). In the Pacific Northwest, aerial applications of 2.2 kg ha⁻¹ ae picloram to a mixture of forests, pastures, and powerline right-of-ways resulted in short-term maximum streamflow concentrations of 20 to 78 mg m⁻³ picloram (Norris, 1969). Similar results were measured with an aerial application of picloram (1.6 to 2.3 kg ha⁻¹ ae) and 2,4-D to six brush-covered watersheds in Oregon (Norris et al., 1982). Hand applications of picloram pellets to riparian vegetation in Arizona (9.0 kg ha⁻¹ ae) on 4.5% of a forest watershed produced stormflow picloram concentrations of 52 to 370 mg m⁻³ for a period of 8 weeks (Davis et al., 1968). Considerably higher concentrations were produced by direct application of liquid picloram to Arizona and Texas streams to study dissipation downstream (Johnsen and Warskow, 1980; Mayeux et al., 1984). Initial concentrations as high as 13 720 mg m⁻³ were diluted to less than 5 mg m⁻³ over 6 km of stream distance. Drainage from a forest plot in Ontario sprayed with 0.9 kg ha⁻¹ ae picloram contained picloram levels of 38 mg m⁻³ one day after application, but still carried small but detectable (< 1 mg m⁻³) amounts 1 yr later (Suffling et al., 1974).

The purpose of this study was to examine picloram persistence and movement in mineral soil, soil solution,

Table 1. General profile description of Porters stony loam, Umbric Dystrochrepts, Watershed 19, Coweeta Hydrologic Laboratory.

Hori-zon	Depth	Description	pH	Perme-ability	Organic matter
	cm			mm h⁻¹	g kg⁻¹
O	5–0	Decomposed organic matter and leaves	4.5–5.5	50–150	
A	0–25	Very dark grayish-brown stony loam	4.5–5.5	50–150	142
Bw1	25–30	Brown stony loam	4.5–5.5	15–50	17
Bw2	30–70	Brown stony loam	4.5–5.0	15–50	13
BC	70–80	Brown loam	4.5–5.0	50–150	†
C	80+	Saprolite, crushes to sandy loam	4.5–5.0	50–150	†

† No data.

springflow, and streamflow within a forest watershed in the Southern Appalachians. The study involved relatively high herbicide rates that were applied on steep topography in a heavy rainfall region of the Southern Appalachians where maximum leaching potential might be expected.

MATERIALS AND METHODS

A portion of the upper slopes of Watershed 19 (WS 19) at the Coweeta Hydrologic Laboratory in western North Carolina was selected for the study. This 28-ha, north-facing watershed ranges in elevation from 792 to 1112 m (Fig. 1). Annual rainfall averages 2054 mm, but can range from 1200 to 2500 mm. Slope, which averages 27% from the weir to the top of WS 19, is typically 35 to 40% on most side slopes, but often exceeds 100% in the upper elevations. The soils are mainly Saluda stony loams, coarse-loamy, mixed, mesic Umbric Dystrochrepts derived from pre-Cambrian gneiss, metasandstone, schist, and quartzite (Table 1). These soils have a fairly high organic matter content in the A horizon. Permeability throughout the profile is rapid, with some reduction in the B horizon. The saprolite has weathered isovolumetrically (30% porosity) and thus does not act as a restrictive layer to drainage (Velbel, 1985). Bedrock occurs at variable depths (2–5 m).

The forest stand is a mixture of low-quality hardwoods dominated by chestnut oak (*Quercus prinus* L.), scarlet oak (*Q. coccinea* Muenchh.), black oak (*Q. velutina* Lam), and hickory (*Carya* spp.). Rhododendron and mountain laurel form an almost impenetrable understory thicket (> 18 000 stems ha⁻¹) which, in some instances, prevents direct sunlight from reaching the forest floor (Neary et al., 1979). This thick understory developed from prolific sprout regrowth after a 22% basal area cut (understory only) in 1949.

On 15 May 1978, picloram herbicide was applied at a rate of 5.0 kg ha⁻¹ ae to two plots, each 2-ha in size, at the head of WS 19 (Fig. 1). To achieve uniform application, the treated area was divided into 25-m² grids and 125 g of the herbicide pellets (10% ae) were broadcast by hand onto each grid. This application rate is about average for control of hardwoods with pelleted picloram (Hamel, 1981). In comparison to where picloram is normally used in combination with 2,4-D, 5.0 kg ha⁻¹ rate used here is nine times the amount of picloram used with 2,4-D.

Hydrologic instrumentation, including water-level recorders, consisted of a 120°, V-notch weir already in place on WS 19 and a temporary 0.3-m H-flume installed at a higher elevation (Fig. 1). The H-flume was equipped with a Coshocton wheel sampler to provide flow-proportional in addition to periodic manual samples (Brakensiek et al., 1979). Two spring heads (S1 and S2, Fig. 1) were selected and deepened to provide access for sampling. The main weir, H-flume, and springs were 760, 200, and 140 m, respectively, below the downslope edge of the picloram treated area. On each of the picloram-treated and the control plots, four sets of porous cup tension lysimeters were installed 8 weeks prior to the picloram application and 15 m uphill from the lower boundary (Fig. 1). Previous research has shown that porous ceramic cups do not adsorb appreciable amounts of picloram (Rao et al., 1974). Each set contained a 0.3-, 0.6-, and 1.2-m-

deep lysimeter sampling from the Bt1, Bt2, and C horizons, respectively. Rainfall data were obtained at the permanent climate station adjacent to WS 17, from temporary storage gages located at the H-flume, and on the watershed divide.

Streamflow sampling started in May, just prior to the picloram application. Manual samples were obtained at both the main weir and H-flume weekly during dry periods, daily during wet periods, and at 1 to 6 h intervals during selected storms producing > 50 mm of precipitation in 24 h. An additional flow-proportional sample was collected continuously from the Coshocton wheel sampling system at the H-flume. Soil solution was sampled with porous cup tension lysimeters (0.02 MPa tension) on a weekly basis (Hansen and Harris, 1975). Periods of drought and winter snowpack caused gaps in the sampling record. All water samples were collected in 1-L glass jars equipped with teflon-lined caps. The bottles were thoroughly washed and rinsed with hexane and acetone prior to use in sampling. Samples were stored at 4°C and extracted for analysis within 7 d.

Mineral soil samples were collected from the two picloram-treated plots (1 and 2 in Fig. 1) after the first rainfall following herbicide application. Sampling continued until mid-December of 1978, Push-tube soil probes were used to collect increments of mineral soil from four depths (0.07, 0.15, 0.22, and 0.30 m) in the upper 0.3 m of the profile. A bucket auger was used to collect 0.1-m increment samples from depths of 0.6 and 1.2 m. Each separately-analyzed sample consisted of ten composites. Mineral soil samples were placed in labeled polyethylene bags in the field and stored frozen prior to analysis. The auger and push-tube probe were rinsed with distilled water between each sample to reduce cross contamination. The bottom and top portions of each bucket sample were also discarded to reduce sample contamination.

Both water and soil samples were transported to the Extension Pesticide Residue Laboratory, Univ. of Georgia, Athens, in insulated and ice-packed containers. Picloram in both water and soil samples was extracted with ether and analyzed by gas-liquid chromatography as the methyl ester (Anonymous, 1968; Anonymous, 1973; Bjerke, 1973). Water samples were acidified with sulfuric acid, extracted with ether and then methylated with diazomethane. Soil was mixed, sub-sampled, extracted with 1 M potassium hydroxide and 10% potassium chloride solvent. Following acidification, picloram was partitioned into the diethyl ether. The ether extract containing the picloram residue was further cleaned using a basic-alumina column chromatography. The picloram residues were methylated with diazomethane and quantified on a gas chromatograph equipped with a ^{63}Ni electron-capture detector. Detection limits were 0.1 mg kg^{-1} for mineral soil and 1.0 mg m^{-3} for water. Trace levels reported in water produced peaks on the gas chromatograms, but were < 1 mg m^{-3} when quantified.

RESULTS AND DISCUSSION

Residues in Mineral Soil

Picloram in the clay pellets was released starting with rainfall 10 d after application. Residues in the upper 0.07 m of mineral soil exhibited a typical dissipation pattern over a 24-week sampling period (Table 2). The initial concentration (11.58 mg kg^{-1}) was determined after the first rainfall 15 d following application. This level was higher than expected (6.0 mg kg^{-1}) based on the theoretical application rate (5.0 kg ha^{-1}). The discrepancy reflects inherent spatial variability in soil bulk density, residue distribution during application, and in sampling mineral soil for pesticide residues. Concentrations of picloram dropped very rapidly in the first 4 weeks as residues were absorbed and translocated into woody vegetation, leached deeper into the soil profile, or degraded by microorganisms. The half-life in the upper 0.07 m, based on these data, was about 4 weeks. This short half-life for picloram is typically found in warm and humid climates. In drier or colder regions, 24-week values are commonly reported (NRCC, 1974).

Table 2. Flux and percent loss of picloram below 1.2 m in a Humic Hapludult soil, Watershed 19, Coweeta Hydrologic Laboratory, May 1978 through December 1979.

Monthly	Actual	Rain Departure from normal	Weighted adjusted ET‡	Water available below 1.2 m†	Picloram Mean conc.	Flux	Loss
		mm			mg m^{-3}	mg m^{-2}	%
1978 May	39	−93	55	0	0.0	0.00	0.00
June	74	−58	117	0	0.0	0.00	0.00
July	29	−121	106	0	0.0§	0.00	0.00
Aug	313	+168	77	100	0.0	0.00	0.00
Sep	40	−82	68	0	1.6	0.00	0.00
Oct	10	−102	58	0	0.6	0.00	0.00
Nov	113	−124	34	3	0.0	0.00	0.00
Dec	185	+12	20	165	5.3	0.87	0.17
1979 Jan	319	+147	18	301	25.5	7.68	1.54
Feb	168	−15	21	147	15.4§	2.26§	0.45
Mar	101	−102	33	68	5.3	0.36	0.07
Apr	231	+84	23	208	4.1	0.85	0.17
May	169	+37	22	147	8.0	1.18	0.24
June	92	−40	88	4	8.0	0.03	0.01
July	234	+84	95	139	9.4	1.31	0.26
Aug	227	+82	90	137	2.8	0.38	0.08
Sep	197	+75	59	138	2.3	0.32	0.06
Oct	134	+22	62	72	2.8	0.20	0.04
Nov	466	+329	38	428	0.4	0.17	0.03
Dec	18	−155	9	9	0.0	0.00	0.00
Total	3159	+148	1093	2066	4.6	15.61	3.12

† Rainfall- monthly ET-accumulated ET deficit.
‡ Based on open pan evapotranspiration, solar radiation, and vegetation cover, Coweeta Hydrologic Laboratory.
§ Estimated.

The mid-June soil concentration (2.21 mg kg^{-1}) did not halve again until 12 weeks later (0.90 mg kg^{-1} in early September). Concentrations declined gradually thereafter reaching 0.06 mg kg^{-1}, close to detection limits (0.01 mg kg^{-1}), 28 to 30 weeks after application. In the upper 0.07 m of mineral soil, the concentration of picloram under these conditions decreased with time according to the site and condition specific empirical equation

$$\ln C_p = 1.6160 - 0.0626\ T_r$$
$$+ 0.006\ T_r^2 - 0.000002\ T_r^3 \qquad r^2 = 0.73 \qquad [1]$$

where
T_r = days from rainfall activation of picloram pellets, and
C_p = picloram concentration in mg kg^{-1}.

Picloram concentrations deeper in the soil profile (0.15 and 0.30 m) initially followed the surface 0.07-m trend. Although initial concentrations were much lower (3.80 and 1.63 mg kg^{-1}) at both depths, concentrations also dropped by more than one-half in the first 4 weeks. Picloram levels in mineral soil at these depths continued to decline by the next sampling occurring in late June. However, by the next sampling periods in August and September, picloram concentrations actually increased by 40 to 150%. In the September sampling, concentrations at 0.15 and 0.22 m exceeded the average concentrations in the surface 0.07 m. Higher picloram concentrations deeper in the soil reflect increased leaching after particularly heavy rainfall in early August (225 mm in 4
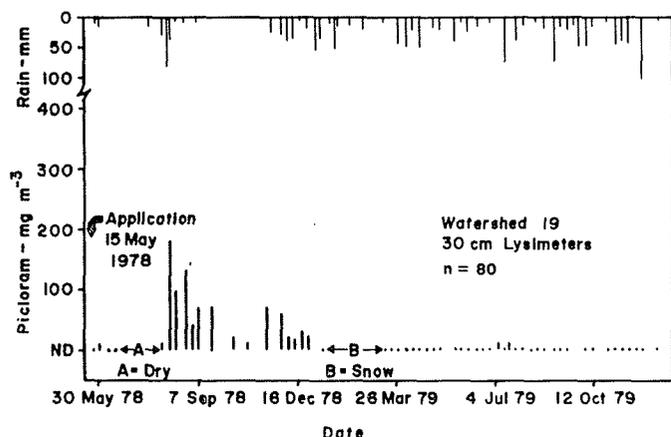
Fig. 2. Mean picloram concentrations in soil solution sampled at 0.3 m in a Humic Hapludult soil, Watershed 19, Coweeta Hydrologic Laboratory, 1978 and 1979.
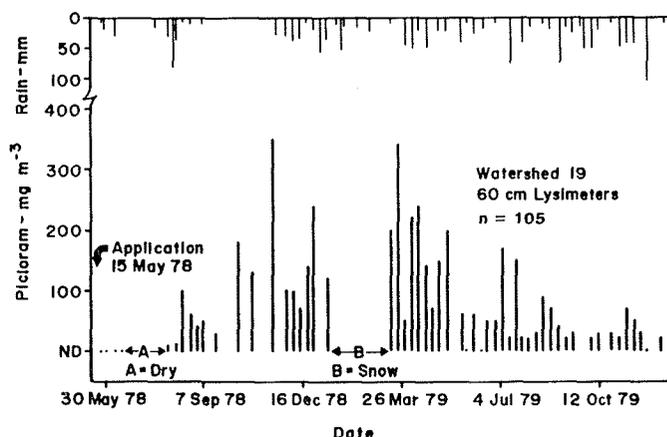

Fig. 3. Mean picloram concentrations in soil solution at 0.6 m in a Humic Hapludult soil, Watershed 19, Coweeta Hydrologic Laboratory, 1978 to 1979.

d). Picloram residues declined thereafter reaching the 0.01 to 0.03 mg kg⁻¹ range by December. At both 0.15 and 0.30 m, the measured concentration of picloram decreased according to Eq. [2] and [3]

$$0.15 \text{ m} \ln C_p = 0.5767 - 0.0436 \ T_r$$
$$+ 0.0006 \ T_r^2 - 0.000002 \ T_r^2 \qquad r^2 = 0.65 \quad [2]$$

$$0.30 \text{ m} \ln C_p = 0.4266 - 0.0400 \ T_r$$
$$+ 0.007 \ T_r^2 - 0.000003 \ T_r^3 \qquad r^2 = 0.74. \quad [3]$$

Where T_r and C_p are as defined in Eq. [1].

Mineral soil samples were not collected at the 0.60- and 1.20-m depths until late June. At that time picloram levels were 34 and 10% of the 0.07-m depth values. The same picloram wave pattern observed in the 0.15 to 0.30-m residue data showed up at 0.60 and 1.20 m. The concentration increases were larger at 0.60 m and delayed longer. The peak picloram concentration (0.86 ± 0.85 mg kg⁻¹) occurred in October and dropped to only half that level by the last sampling date. Picloram concentrations at 1.20 m remained relatively low (< 0.13 ± 0.23 mg kg⁻¹) but showed the effects of the downward leaching of the chemical.

Picloram residues measured in mineral soil samples represented the chemical adsorbed onto organic matter, mineral surfaces coated with organic matter, and clay exchange sites, plus residues in soil solution. The Humic Hapludult soils with high organic matter surface horizons (75 g kg⁻¹ C) and high clay content in the subsoil were apparently effective in containing much of the picloram on the application site. On-site retention was visually evident in the treated hardwood stand by the clearly defined downslope treatment boundary.

Trees immediately downslope (60 to 100% slopes) of the picloram-treated area did not show any indication of picloram herbicidal activity. Vegetative uptake of picloram in the treated area was considerable despite dry weather conditions which limited the chemical's effectiveness (Neary et al., 1979). Picloram levels in the upper 0.3 m of mineral soil, although not determined after December 1978, were not high enough the follow-

ing March to cause mortality of any planted white pine (Neary et al., 1984).

Residues in Soil Solution

Vertical movement of water due to gravity is the major mechanism for offsite movement of picloram in WS 19. Lateral flow would occur only where picloram residues reached unweathered rocks below the rhizosphere. Surface runoff is a rare phenomenon in the deep well-drained Hapludult soils of the Southern Appalachians (Hewlett and Hibbert, 1967). Also, isovolumetric weathering of saprolite below the developed soil tends to produce deep water flow rather than shallow interflow (Velbel, 1985). Porous-cup tension lysimeters were installed to sample water just above the zone of clay (argillic) accumulation (0.3-m depth), within the argillic horizon (0.6-m depth), and in saprolite material (1.2-m depth) (Table 1).

Very small amounts of picloram were initially transported in soil solution, probably moving via unsaturated flow in the large macropores characteristic of these Umbric Dystrochrept soils at 0.3 m (Fig. 2). Droughty conditions in June and July 1978 precluded soil solution sampling ("A" in Fig. 2). Increased precipitation in August produced the highest pulse of picloram at 0.3 m (mean concentration of 174 mg m⁻³ with an individual maximum of 246 mg m⁻³). Concentrations declined thereafter, with a smaller pulse of picloram residues in November 1978 (60-80 mg m⁻³). During the winter months of 1979, soil solution samples were not collected because of snow conditions ("B" in Fig. 2). Sampling resumed in March 1979, but picloram residues were not detectable (detection limit 1 mg m⁻³) until July. Then several small amounts of picloram (5-15 mg m⁻³) were measured in soil solution at 0.3 m. Picloram residues were not detected after July 1979.

At 0.6 m, within the Bw2 horizon, picloram residues were not detected until after the summer drought ended ("A" on Fig. 3). A pulse of residues with peak concentration < 100 mg m⁻³ occurred after the early August 1978 storm. Picloram concentrations at 0.6 m declined briefly, then rose sharply in October (180 mg m⁻³) and November (350 mg m⁻³). An increase in rainfall
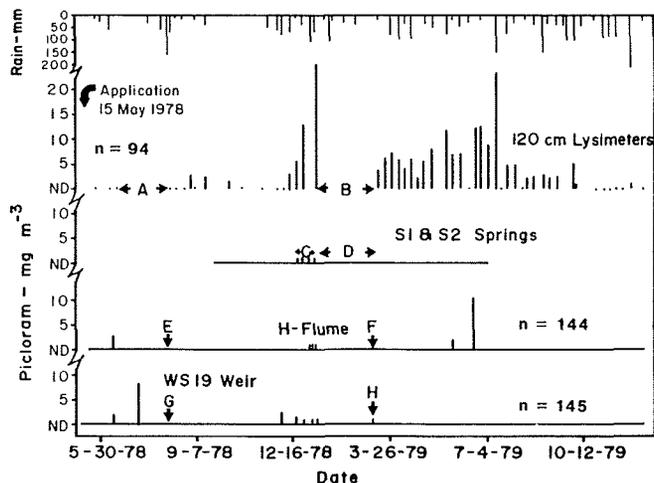
Fig. 4. Mean picloram concentrations in soil solution at 1.2 m in a Humic Hapludult soil, in springflow, and at two gaging stations, Watershed 19, Coweeta Hydrologic Laboratory, 1978 to 1979.

frequency in late November and during December kept soil solution concentrations in the 100 to 250 mg m⁻³ range until sampling stopped for the winter ("B" in Fig. 3). After sampling resumed in March 1979, picloram peaked in soil solution, with a mean concentration of 381 mg m⁻³. Thereafter concentrations gradually declined, with frequent pulses of 100 to 200 mg m⁻³. At the end of sampling in mid-December 1979, soil solution at the 0.6-m depth was carrying 25 mg m⁻³ picloram.

Few samples collected in the saprolite at 1.2 m contained more than 10 mg m⁻³ of the herbicide (top, Fig. 4). Picloram was first detected in early September 1978 at a concentration of 2 mg m⁻³, but was frequently not detectable. At the end of December 1978 and during June and July 1979, mean concentrations exceeded 10 mg m⁻³, but did not go over 25 mg m⁻³. Picloram residues at 1.2 m were characterized by a high degree of variability, since 50% of the samples on a given date did not contain detectable levels. Also, the low picloram concentrations from 1.2 m plotted in Figure 4 at the same scale as the other two depths (Fig. 2 and 3) would appear to be mainly nondetectable and featureless. At 1.2 m, picloram residues in soil solution did show a concentration pulse pattern similar to that seen at 0.3 and 0.6 m. However, concentrations were one order of magnitude lower and delayed in time. This time lag is the same as that previously reported by Hewlett (1966) for unsaturated flow in the lower soil profile.

Picloram residues in soil solution at 0.3 m were probably affected by variability in surface application of the herbicide pellets and rapid flow in macropores. At 0.6 m, picloram concentrations in unsaturated flow were higher than at 0.3 m, since residues had more time and space to diffuse out into slower moving soil water. Evidently, the 0.6 m of soil material between the two lower lysimeter depths was sufficient to adsorb small, but significant, amounts of picloram. Concentrations at 1.2 m were at most 10% of those at 0.6 m. One hypothesis for this concentration reduction would be lateral interflow along the top of the Bt2 horizon. This process could divert soil water with higher picloram residues away from the 1.2-m-deep lysimeters and downslope into the root systems of untreated vegeta-

tion. There was no physical evidence to indicate major interflow occurred (Hewlett and Hibbert, 1967) and evergreen vegetation downslope of the herbicide treatment boundary did not show phytotoxic symptoms. Thus, the lateral movement mechanism was judged not important in reducing picloram residues in soil solution between 0.6 and 1.2 m.

Flux of picloram in unsaturated water flow in the saprolite below 1.2 m was estimated using a procedure described by Troendle and Leaf (1980). Rainfall, adjusted evapotranspiration, water available for flow below 1.2 m, and mean monthly picloram concentration were used to calculate picloram flux (Table 2). Picloram concentrations below detection limits and dry conditions precluded movement below 1.2 m until December 1978. The largest flux, according to these estimates, would have occurred in January and February 1975. Net movement of picloram was likely during all but the last month of 1979. The total estimated loss below 1.2 m, 3.12% of the applied picloram, agrees with losses of herbicides reported elsewhere (Wauchope, 1978).

Springflow Residues

A major water quality concern with picloram is its high solubility and potential to move offsite into streams or groundwater. Thus, two springs (S1 and S2) below the picloram-treated area were sampled to determine if residues were migrating downslope in saturated flow at the saprolite-bedrock interface (Fig. 1). These two springs, 140 m downslope of the picloram-treated area, mark the beginning of perennial flow for 40 to 50% of the eastern side of WS 19. Such springs are sometimes used for domestic sources of water in the Appalachian Mountains. Flow from both springs is eventually routed through the H-flume to the main gaging station (Fig. 1).

Both springs were deepened to enable sample collection and to observe flow from the saturated soil mantle. Neither spring was measured to determine flow rates. Sampling started in October 1978 on a weekly basis.

No picloram residues were measured until 20 December 1978 when traces of picloram began appearing. Trace levels were present in S1 or S2 until 8 January 1979 ("C" in Fig. 4). The sampling frequency was increased to once every 2 to 3 d, from early January to late March 1979 ("D" in Fig. 4). Twenty-eight samples were collected from both S1 and S2 during this period and no additional picloram residues were detected in springflow. Sampling resumed at a normal weekly or biweekly interval until July 1979 when springflow sampling ceased. During this period also, picloram residues were not detectable in either spring.

During the 40 weeks that springs S1 and S2 were monitored, picloram residues were present in only trace levels for a period of 18 days. In terms of water quality impacts, there was no adverse effect on the quality of the springs. The residue levels were below those needed to impact the most sensitive vegetable crops (1 to 10 mg m⁻³) and were short in duration. No human exposure standards have been set by the Environmental Protection Agency for picloram residues in water because of the compund's low toxicity and lack of bioaccumulation (Anonymous, 1976). A chronic SNARL (Suggested No

Table 3. Mean picloram residues in a Typic Hapludult soil during 27 weeks after application, Watershed 19, Coweeta Hydrologic Laboratory.

Depth	Picloram concentrations in mineral soil						
	31 May 1978†	12 June 1978	26 June 1978	14 Aug. 1978	8 Sept. 1978	5 Oct. 1978	18 Dec. 1978
m				mg kg⁻¹			
0.07	11.58 ± 1.19‡	2.21 ± 0.77	1.31 ± 0.44	1.27 ± 0.62	0.90 ± 0.37	0.34 ± 0.05	0.06 ± 0.03
0.15	3.80 ± 3.05	1.42 ± 0.48	1.17 ± 0.43	0.83 ± 0.29	1.16 ± 0.34	0.75 ± 0.35	0.03 ± 0.01
0.22	¶	0.98 ± 0.21	0.49 ± 0.07	0.80 ± 0.45	1.23 ± 0.31	0.34 ± 0.12	0.01 ± 0.01
0.30	1.63 ± 1.33	0.45 ± 0.23	0.38 ± 0.12	0.62 ± 0.25	0.81 ± 0.28	0.53 ± 0.19	0.01 ± 0.01
0.60	¶	¶	0.45 ± 0.44	0.08 ± 0.06	0.48 ± 0.26	0.86 ± 0.43	0.40 ± 0.28
1.20	¶	¶	0.13 ± 0.12	ND ± 0.00§	0.11 ± 0.09	0.01 ± 0.01	

† Sampling date 1 d after first rain. Application date 15 May 1978.
‡ Means ± standard error.
§ Detection limit 0.01 mg kg⁻¹.
¶ Samples not taken at this depth.

Adverse Response Level) of 1050 mg m⁻³ has been recommended by the Safe Drinking Water Committee of the National Research Council (NRC, 1983). The tolerance level for milk (50 mg m⁻³) is 50 to 100 times the levels observed in springflow. By comparison, the tolerance level for 2,4-D in municipal water supplies is 100 mg m⁻³.

Residues in Streamflow-10 ha Watershed

Picloram movement in streamflow was monitored at an H-flume sampling station below the herbicide treated area and the 120° V-notch weir at the base of the watershed (Fig. 1). These two streamflow gaging stations encompass watersheds of 10 and 28 ha, respectively. Mean daily flows at the H-flume were 0.007 to 0.011 m³ s⁻¹ km⁻² in low flow periods (October-November) and 0.033 to 0.109 m³ s⁻¹ km⁻² in high flow periods (March–April). The instantaneous peakflow at the H-flume (0.296 m³ s⁻¹ km⁻²) occurred during the early August 1978 storm, which was the first major storm event after picloram application (Fig. 4).

At the H-flume, two sampling techniques were employed. A Coshocton wheel attached to the flume produced a 0.5% flow-proportional sample. In addition, grab samples were collected weekly or on a more frequent basis as conditions warranted. Of 75 samples collected on a flow-proportional basis between 22 May 1978 and 14 September 1979, only one sample had a trace of picloram. As will be shown with manually-collected samples, picloram residue pulses were so sporadic and so low in concentration that the flow-proportional bulking process diluted any picloram levels below detection limits. Data from the H-flume presented in Fig. 4 are from the manually collected discrete samples rather than the flow-proportional ones.

Of 144 discrete samples collected at the WS 19 H-flume, only a few had any positive picloram residues (Fig. 4). One, on 9 June 1978, contained 3 mg m⁻³ picloram. Except for several samples in early January 1979, picloram residues in streamflow at the flume did not show any pattern related to residue levels higher up in the watershed.

A series of frequent samples were collected at the H-flume during the rainfall in early August which constituted the first major storm event after the picloram application in May ("E" in Fig. 4). One sample was taken daily from 1 through 6 August. Then, five samples were collected on 7 August 1978 at 2- to 4-h

intervals from 0800 to 1915 hours during the peak stormflow of this entire study. Daily sampling resumed during the period of 8 August through 10 August. Throughout all this intensive sampling no picloram residues were detected in streamflow.

Samples continued to be negative for picloram until January 1979 when three consecutive samples on 2, 3, and 8 January had trace levels. During March, another set of closely-spaced samples was collected daily from 2 March through 9 March 1979. However, all samples were negative for picloram residues ("F" in Fig. 4). Only two more samples, collected on 30 May and 20 June 1979, had picloram levels of 2 and 10 mg m⁻³, respectively. The appearance of these two small pulses could be related to an additional flux of picloram out of the soil system in May (Table 3). Another flux of picloram in July 1979 did not produce detectable residues at the H-flume. Sampling through mid-December 1979 failed to turn up any additional picloram.

Residues in Streamflow- 28-ha Watershed

Streamflow samples collected further downstream at the main weir on WS 19 (Fig. 1) showed the same pattern as that observed at the H-flume (Fig. 1). A total of 145 discrete samples were collected manually between 12 May 1978 and 13 December 1979. A small amount of picloram (2 mg m⁻³) was measured in a sample collected 3 d after (12 June 1978) the one which was positive at the H-flume (3 mg m⁻³). Another sample collected in early July had 8 mg m⁻³. Both of these samples were collected after rainfall (Fig. 4) but were not associated with significant residue movement elsewhere in the watershed. The latter peak may have passed through the H-flume but was missed by the grab sampling and diluted by the continuous flow-proportional sampling. Intensive sampling ("G" in Fig. 4) during the August storms, similar to that described for the H-flume site, did not turn up any picloram residues.

A series of samples collected at the WS 19 weir in December 1978 and January 1979 contained intermittent picloram residues in the trace to 2 mg m⁻³ range. Streamflow samples thereafter were mostly free of picloram. One sample taken during intensive sampling in March 1979 ("H" in Fig. 4) contained a trace amount of picloram.

Although very low-level residues of picloram were detected at the WS 19 weir and probably continued on into Ball Creek, they were so infrequent and at such low

levels as to have no adverse effect on the quality and subsequent uses of water downstream. Mixing of flow from the WS 19 stream (Snake Den Branch) with flow from the larger Ball Creek (Fig. 1) would undoubtedly reduce the observed concentrations of picloram well below detection limits.

CONCLUSIONS

The application of a pellet formulation of picloram to 4 ha of ridge and upper slopes of a 28 ha Appalachian Mountain forest watershed did not produce any adverse affect on water quality within the 2 years of the study. Picloram in the upper 0.07 m of mineral soil exhibited a very short half-life (4 weeks) compared to other reported values. Concentrations in the upper 0.3 m of mineral soil were close to detection limits after 28 to 30 weeks. Although soil solution concentrations reached 381 mg m^{-3}, picloram was at or near detection limits some 60 weeks after application. These high concentrations did not carry on downslope in springflow or streamflow. Residues of this highly soluble, and hence mobile, herbicide were observed considerable distances (700–800 m) downstream. However, levels were low (10 mg m^{-3}) and very sporadic.

There has been considerable concern about the use of picloram for silvicultural treatments in the high rainfall zone of the Appalachians. The picloram application rate used in this study was 9 times that of the most commonly used picloram forest-use herbicide (2,4-D plus picloram). When used at rates established on the product label in accordance with special use precautions and well away from flowing streams, picloram should not pose any threat to water quality. The pelleted formulation is easy to control during application and thus less susceptible to accidental movement into streams. In addition, picloram is very low in toxicity to aquatic fauna. Use of picloram as described in this study is one alternative for site preparation and weed control in the steeplands of the Appalachian Mountains. We believe that this method is practical, does not disturb soil, and does not pose a significant adverse impact on the aquatic environment and water quality.

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